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(54) **NEGATIVE ELECTRODE ACTIVE SUBSTANCE MATERIAL, NEGATIVE ELECTRODE, AND CELL**

NEGATIVELEKTRODEN-AKTIVMATERIAL, NEGATIVELEKTRODE UND ZELLE

MATÉRIAU DE SUBSTANCE ACTIVE D'ÉLECTRODE NÉGATIVE, ÉLECTRODE NÉGATIVE ET CELLULE

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Description

TECHNICAL FIELD

[0001] The present invention relates to an electrode active material, and more particularly to a negative electrode active material.

BACKGROUND ART

[0002] Recently, small electronic appliances such as home video cameras, note PCs, and smart phones have become widespread, and attaining higher capacity and longer service life of batteries has become a technical problem.

[0003] Given that hybrid vehicles, plug-in hybrid vehicles, and electric vehicles will be further spread, size reduction of batteries is also a technical problem.

[0004] At present, graphite-based negative electrode active materials are utilized for lithium ion batteries. However, graphite-based negative electrode active materials have technical problem as described above.

[0005] Accordingly, alloy-based negative electrode active materials have gained attention, which have higher capacity than those of the graphite-based negative electrode active materials. As an alloy-based negative electrode active material, silicon (Si)-based negative electrode active materials and tin (Sn)-based negative electrode active materials are known. To realize a lithium ion battery having a smaller size and a longer life, various studies have been conducted on the above described alloy-based negative electrode active materials.

[0006] However, an alloy-based negative electrode active material repeatedly undergoes large expansion and contraction in volume at the time of charging/discharging. For that reason, the capacity of the alloy-based negative electrode active material is prone to deteriorate. For example, a volume expansion/contraction ratio of graphite associated with charging is about 12%. In contrast, the volume expansion/contraction ratio of Si single substance or Sn single substance associated with charging is about 400%. For this reason, if a negative electrode plate of Si single substance or Sn single substance is repeatedly subjected to charging and discharging, significant expansion and contraction occur, thereby causing cracking in negative electrode mixture which is applied on the current collector of the negative electrode plate. Consequently, the capacity of the negative electrode plate sharply decreases. This is chiefly caused by the fact that some of the active substances are freed due to volume expansion/contraction and thereby the negative electrode plate loses electron conductivity.

[0007] US2008/0233479A (Patent Literature 1) proposes a method for solving the above described problem of an alloy-based negative electrode active material. To be specific, the negative electrode material of Patent Literature 1 includes a Ti-Ni superelastic alloy, and Si particles formed in the superelastic alloy. Patent Literature 1 describes that a large expansion/contraction change of Si particle which occur following occlusion and release of lithium ions can be suppressed by a superelastic alloy.

[0008] JP 2011 032541 discloses a nanosize particle containing an element A-1 and an element A-2 as two kinds of elements selected from the group consisting of Si, Sn, Al, Pb, Sb, Bi, Ge, In and Zn, which has a first phase as the single substance or solid solution of the element A-1 and a second phase as the simple substance or solid solution of the element A-2. Both of the first phase and the second phase are exposed to the outer surfaces, and the outer surfaces of the first phase and the second phase are non-spherical. The negative electrode material for a lithium ion secondary battery uses the nanosize particle.

[0009] US 2013/084498 discloses a negative electrode active material including an Si-Sn-Fe-Cu based alloy, in which an Si phase has an area ratio in a range of from 35 to 80% in the entire negative electrode active material, the Si phase is dispersed in a matrix phase, the matrix phase contains an Si-Fe compound phase crystallized around the Si phase and further contains an Sn-Cu compound phase crystallized to surround the Si phase and the Si-Fe compound phase, the Si-Fe compound phase is crystallized in a ratio of from 35 to 90% in terms of an area ratio in the entire matrix phase, and the matrix phase further contains an Sn phase unavoidably crystallized in the matrix phase in a ratio of 15% or less in terms of an area ratio in the entire matrix phase.

[0010] US 2012/082895 discloses a negative electrode active material for a lithium secondary battery, which has a composition containing Si in an amount of from 30 to 65% by mass and has a two phase matrix structure including an Sn-Cu based alloy matrix having an Sn content of 50% by mass or more, Si crystallites dispersed in the Sn-Cu based alloy matrix and an Si-X based alloy crystallized so as to at least partially cover the Si crystallites, in which X is at least one element selected from Fe, Ni and Co and is added in the Si-X based alloy in an amount of 1% by mass or more.

[0011] US 2007/111094 discloses a method of making an intermetallic negative electrode for an electrochemical cell. One or more metal salts is dissolved in an organic solvent forming a solution to which is added a metal reducing agent to form an intermetallic compound. Thereafter, the intermetallic compound precipitates and is separated and formed into an electrode. The electrodes are useful in electrochemical cells and batteries.

[0012] JP 2010 261078 discloses an anode active material of the nonaqueous electrolyte secondary cell, solid solution

represented by formula (1): $Li_xM^1_yM^2_z$ is used. (1) (wherein M^1 is at least one element selected from a group consisting of Ti, Zr, Mn, Co, Ni, Cu and Fe, and M^2 is at least one element selected from a group consisting of Si and Sn, $0 \leq x < 10$, $0.1 \leq y \leq 10$, and $z=1$).

[0013] JP 2001 243946 discloses a nonaqueous electrolyte secondary cell made of compound particles with the structure that the whole or partial area surrounding core particles of solid phase A, composed of at least one element out of Si, Sn or Zn, is covered by a solid phase B, here, the solid phase B is composed of solid solution or intermetallic compound of one of Si, Sn, Zn composing the solid phase A, and an element chosen from group 2 elements, transition elements, or group 12, 13, and 14 elements of periodic table (except the elements constituting the solid phase A and carbon). The compound particles include 1-50 weight % of ceramics.

CITATION LIST

PATENT LITERATURE

[0014] Patent Literature 1: US2008/0233479A

[0015] However, it is dubious that the technique disclosed in Patent Literature 1 sufficiently improves the charge-discharge cycle characteristics of the secondary battery. Most of all, it may be highly difficult to actually produce the negative electrode active material proposed by Patent Literature 1.

SUMMARY OF INVENTION

[0016] It is an objective of the present invention to provide a negative electrode active material which can improve the discharge capacity per volume and/or charge-discharge cycle characteristics thereof.

[0017] The negative electrode active material according to the present is defined in the appended claims.

[0018] The negative electrode active material of the present embodiment can improve the discharge capacity per volume and/or the charge-discharge cycle characteristics.

BRIEF DESCRIPTION OF DRAWINGS

[0019]

[FIG. 1] FIG. 1 is a perspective view of $D0_3$ structure.
[FIG. 2A] FIG. 2A is a schematic diagram of $D0_3$ structure of the matrix phase of the alloy phase of the present embodiment.
[FIG. 2B] FIG. 2B is a schematic diagram of 2H structure of $\gamma 1'$ phase which is a kind of martensite phase.
[FIG. 2C] FIG. 2C is a schematic diagram of a crystal plane to explain thermoelastic diffusionless transformation from $D0_3$ structure to 2H structure.
[FIG. 2D] FIG. 2D is a schematic diagram of another crystal plane different from that of FIG. 2C.
[FIG. 2E] FIG. 2E is a schematic diagram of another crystal plane different from those of FIGS. 2C and 2D.

DESCRIPTION OF EMBODIMENTS

[0020] Hereinafter, with reference to the drawings, embodiments of the present invention will be described in detail. Like parts or corresponding parts in the drawings are given a like reference symbol and description thereof will not be repeated.

[0021] The negative electrode active material according to the present embodiment contains an alloy phase and ceramics and is according to the claims.

[0022] A "negative electrode active material" referred herein is preferably a negative electrode active material for nonaqueous electrolyte secondary batteries. A "thermoelastic diffusionless transformation" referred herein is so-called thermoelastic martensitic transformation. A "metal ion" refers to, for example, a lithium ion, magnesium ion, sodium ion, and the like. A preferable metal ion is lithium ion.

[0023] This negative electrode active material may contain other phases different from the above described alloy phases. The other phases include, for example, a silicon (Si) phase, a tin (Sn) phase, other alloy phases (alloy phases which do not undergo thermoelastic diffusionless transformation) excepting the above described alloy phases, and the like.

[0024] Preferably, the above described alloy phases are main components (main phases) of the negative electrode active material. "Main component" refers to a component which occupies not less than 50% by volume. The alloy phase may contain impurities. However, the impurities are contained preferably as little as possible.

[0025] A negative electrode formed of a negative electrode active material of the present embodiment has a higher volumetric discharge capacity (discharge capacity per volume) than that of a negative electrode made of graphite, when used in a nonaqueous electrolyte secondary battery. Further, a nonaqueous electrolyte secondary battery using a negative electrode containing a negative electrode active material of the present embodiment has a higher capacity retention ratio than one using a conventional alloy-based negative electrode. Therefore, the negative electrode active material can sufficiently improve the charge-discharge cycle characteristics of the nonaqueous electrolyte secondary battery.

[0026] A possible reason why the capacity retention ratio is high is that strain due to expansion/contraction that occurs at the time of charging/discharging is relaxed by thermoelastic diffusionless transformation. Moreover, it is considered that containing a specific amount of ceramics dispersed in the alloy phase contributes to a high capacity retention ratio. Detailed description thereof will be given below.

[0027] The ceramics preferably contains at least one or more kinds selected from the group consisting of Al_2O_3, FeSi, SiC, Si_3N_4, TiC, TiB_2, Y_2O_3, ZrB_2, HfB_2, ZrO_2, ZnO, WC, W_2C, CrB_2, BN, and CeO_2.

[0028] The alloy phase may be of any one of the following types 1 to 4.

[0029] The alloy phase of type 1 undergoes thermoelastic diffusionless transformation when occluding metal ions, and undergoes reverse transformation when releasing metal ions. In this case, the alloy phase is a mother phase in a normal state.

[0030] The alloy phase of type 2 undergoes reverse transformation when occluding metal ions, and undergoes thermoelastic diffusionless transformation when releasing metal ions. In this case, the alloy phase is a martensite phase in a normal state.

[0031] The alloy phase of type 3 undergoes supplemental deformation (slip deformation or twin deformation) when occluding metal ions, and returns to the original martensite phase when releasing metal ions. In this case, the alloy phase is a martensite phase in a normal state.

[0032] The alloy phase of type 4 transforms from a martensite phase to another martensite phase when occluding metal ions, and returns to the original martensite phase when releasing metal ions. In this case, the alloy phase is a martensite phase in a normal state.

[0033] In the case of the alloy phase of type 1, preferably, the crystal structure of the alloy phase after thermoelastic diffusionless transformation is either of 2H, 3R, 6R, 9R, 18R, M2H, M3R, M6R, M9R, and M18R in the Ramsdell notation, and the crystal structure of the alloy phase after reverse transformation is $D0_3$ in the Strukturbericht notation. More preferably, the crystal structure of the alloy phase after thermoelastic diffusionless transformation is the above described 2H, and the crystal structure of the alloy phase after reverse transformation is the above described $D0_3$.

[0034] In the case of the alloy phase of type 1, preferably, the alloy phase contains Cu and Sn, and also contains the above described 2H structure after thermoelastic diffusionless transformation, and the above described $D0_3$ structure after reverse transformation.

[0035] The above described alloy phase may contain one or more selected from the group consisting of Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Al, Si, B, and C, and Sn, with balance being Cu and impurities.

[0036] The above described alloy phase may contain one or more selected from the group consisting of δ phase of F-Cell structure, ε phase of 2H structure, η' phase of monoclinic crystal, and a phase having $D0_3$ structure, each including site deficiency.

[0037] All of these δ phase, ε phase, η' phase, and phase having $D0_3$ structure, each including site deficiency form a storage site and a diffusion site of metal ions (Li ions, etc.) in the alloy phase. Thereby, the volumetric discharge capacity and the cycle characteristics of the negative electrode active material are further improved.

[0038] In the above described negative electrode active material, a volume expansion ratio or volume contraction ratio of a unit cell of the above described alloy phase before and after the phase transformation is preferably not more than 20%, and more preferably not more than 10%. The volume expansion ratio of unit cell is defined by the following Formula (1), and the volume contraction ratio of unit cell is defined by the following Formula (2).

$$\text{(Volume expansion ratio of unit cell)} = [\text{(volume of unit cell when metal ions are occluded)} - \text{(volume of unit cell when metal ions are released)}]/\text{(volume of unit cell when metal ions are released)} \times 100 \quad \ldots(1)$$

$$\text{(Volume contraction ratio of unit cell)} = [\text{(volume of unit cell when metal ions are occluded)} - \text{(volume of unit cell when metal ions are released)}]/\text{(volume of unit cell when metal ions are occluded)} \times 100 \quad \ldots(2)$$

[0039] The volume of unit cell at the time of releasing, which corresponds to a crystal lattice range of unit cell at the time of occluding, is substituted into "volume of unit cell when metal ions are released" in Formulas (1) and (2).

[0040] The above described negative electrode active material can be used as active material for making up an electrode, particularly electrode of a nonaqueous electrolyte secondary battery. An example of the nonaqueous electrolyte secondary battery is a lithium ion secondary battery.

[0041] Hereinafter, negative electrode active materials according to the present embodiment will be described in detail.

<Negative electrode active material>

[0042] The negative electrode active material according to the present embodiment contains an alloy phase and ceramics and is defined in the claims. The ceramics is dispersed in the alloy phase. The content of ceramics in the alloy phase is more than 0 to 50 mass% with respect to the total mass of the alloy phase and the ceramics.

[Alloy Phase]

[0043] The alloy phase undergoes thermoelastic diffusionless transformation when releasing metal ions represented by Li ions, or occluding the metal ions, as described above. The thermoelastic diffusionless transformation is also called as thermoelastic martensitic transformation. Hereinafter, in the present description, the thermoelastic martensitic transformation is simply referred to as "M transformation" and the martensite phase as "M phase". An alloy phase that undergoes M transformation when occluding or releasing metal ions is also referred to as a "specific alloy phase".

[0044] The specific alloy phase is dominantly made up of at least one of M phase and a matrix phase. The specific alloy phase repeats occlusion/release of metal ions at the time of charging/discharging. Then, the specific alloy phase undergoes M transformation, reverse transformation, supplemental deformation, etc. in response to occlusion and release of metal ions. These transformation behaviors mitigate strain which is caused by expansion and contraction of the alloy phase when occluding and releasing metal ions.

[0045] The specific alloy phase may be of any one of the above described types 1 to 4. Preferably, the specific alloy phase is of type 1. That is, the specific alloy phase preferably undergoes M transformation when occluding metal ions, and undergoes reverse transformation when releasing metal ions.

[0046] The crystal structure of the specific alloy phase is not specifically limited. If the alloy phase is of type 1, and the crystal structure of the specific alloy phase (that is, a matrix phase) after reverse transformation is β_1 phase ($D0_3$ structure), the crystal structure of the specific alloy phase (that is, M phase) after M transformation is, for example, β_1' phase ($M18R_1$ structure of monoclinic crystal or $18R_1$ structure of orthorhombic crystal), γ_1' phase (M2H structure of monoclinic crystal or 2H structure of orthorhombic crystal), β_1" phase ($M18R_2$ structure of monoclinic crystal or $18R_2$ structure of orthorhombic crystal), α_1' phase (M6R structure of monoclinic crystal or 6R structure of orthorhombic crystal), and the like.

[0047] If the crystal structure of the matrix phase of the specific alloy phase is β_2 phase (B2 structure), the crystal structure of M phase of the specific alloy phase is, for example, β_2' phase (M9R structure of monoclinic crystal or 9R structure of orthorhombic crystal), γ_2' phase (M2H structure of monoclinic crystal or 2H structure of orthorhombic crystal), and (α_2' phase (M3R structure of monoclinic crystal or 3R structure of orthorhombic crystal).

[0048] If the matrix phase of the alloy phase has a face-centered cubic lattice, the crystal structure of M phase of the alloy phase has, for example, a face-centered tetragonal lattice, and a body-centered tetragonal lattice.

[0049] Such symbols as the above described 2H, 3R, 6R, 9R, 18R, M2H, M3R, M6R, M9R, and M18R are used as the method of denoting crystal structures of a layered construction according to Ramsdell's classification. The symbols H and R mean that respective symmetries in the direction perpendicular to the lamination plane are hexagonal symmetry and rhombohedral symmetry. If there is no M appended at the beginning, it means that the crystal structure is an orthorhombic crystal. If there is M appended at the beginning, it means that the crystal structure is a monoclinic crystal. Even if same classification symbols are used, there are cases in which distinction is made by the difference in the order of the layers. For example, since β_1' phase and β_1" phase, which are two kinds of M phase, have a different layered construction, there are cases in which they are distinguished by being denoted as $18R_1$ and $18R_2$, or $M18R_1$ and $M18R_2$ etc., respectively.

[0050] In General, M transformation and reverse transformation in normal shape memory effects and pseudoelastic effects often involve volume contraction or volume expansion. When the alloy phase of a negative electrode active material relating to the present embodiment electrochemically releases or occludes metal ions (for example, lithium ions), it is considered that the crystal structure often changes in consistent with the phenomena of volume contraction or volume expansion in the direction of respective transformation.

[0051] However, the negative electrode active material according to the present embodiment will not be particularly limited by such restriction. When M transformation or reverse transformation occurs following occlusion and release of metal ions in the specific alloy phase, there may be generated other crystal structures than the crystal structure that

appears at the time of ordinary shape memory effects and pseudoelastic effects.

[0052] When the specific alloy phase is of type 3, the specific alloy phase undergoes slip deformation or twin deformation following occlusion or release of metal ions. In slip deformation, since dislocation is introduced as the lattice defect, reversible deformation is difficult. Therefore, when the specific alloy phase is of type 3, it is preferable that twin deformation dominantly occurs.

[Chemical Composition Of Alloy Phase]

[0053] The chemical composition of the above described specific alloy phase is such that the crystal structure at the time of M transformation and reverse transformation contains the above described crystal structures.

[0054] When the specific alloy phase is of type 1, the chemical composition of the specific alloy phase contains Cu (copper) and Sn (tin).

[0055] When the specific alloy phase is of type 1, the crystal structure of the specific alloy phase after reverse transformation caused by discharge of metal ions is $D0_3$ structure shown in FIG. 1, and the crystal structure of the specific alloy phase after M transformation caused by occlusion of metal ions is 2H structure.

[0056] The chemical composition of a specific alloy phase contains 10 to 20 at% or 21 to 27 at% of Sn, with the balance being Cu and impurities, wherein the negative electrode active material contains 2H structure after M transformation, and $D0_3$ structure after reverse transformation. A preferable Sn content in the alloy phase is 13 to 16 at%, 18.5 to 20 at%, or 21 to 27 at%.

[0057] The chemical composition of a specific alloy phase contains one or more selected from the group consisting of Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Al, Si, B, and C, and Sn, with the balance being Cu and impurities.

[0058] The chemical composition of the specific alloy phase in this case contains: Sn: 10 to 35 at%, and one or more selected from the group consisting of Ti: 9.0 at% or less, V: 49.0 at% or less, Cr: 49.0 at% or less, Mn: 9. 0 at% or less, Fe: 49.0 at% or less, Co: 49.0 at% or less, Ni: 9.0 at% or less, Zn: 29.0 at% or less, Al: 49.0 at% or less, Si: 49.0 at% or less, B: 5.0 at% or less, and C: 5.0 at% or less, with the balance being Cu and impurities. The above described Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Al, Si, B and C are optional elements.

[0059] The upper limit of Ti content is 9.0 at% as described above. The upper limit of Ti content is preferably 6.0 at%, and more preferably 5.0 at%. A lower limit of Ti content is preferably 0.1 at%, more preferably 0.5 at%, and further preferably at 1.0 at%.

[0060] The upper limit of V content is 49.0 at% as described above. The upper limit of V content is preferably 30.0 at%, more preferably 15.0 at%, and furthermore preferably 10.0 at%. A lower limit of V content is preferably 0.1 at%, more preferably 0.5 at%, and further preferably at 1.0 at%.

[0061] The upper limit of Cr content is 49.0 at% as described above. The upper limit of Cr content is preferably 30.0 at%, more preferably 15.0 at%, and furthermore preferably 10.0 at%. A lower limit of Cr content is preferably 0.1 at%, more preferably 0.5 at%, and further preferably at 1.0 at%.

[0062] The upper limit of Mn content is 9.0 at% as described above. The upper limit of Mn content is preferably 6.0 at%, and more preferably 5.0 at%. A lower limit of Mn content is preferably 0.1 at%, more preferably 0.5 at%, and further preferably at 1.0 at%.

[0063] The upper limit of Fe content is 49.0 at% as described above. The upper limit of Fe content is preferably 30.0 at%, more preferably 15.0 at%, and furthermore preferably 10.0 at%. A lower limit of Fe content is preferably 0.1 at%, more preferably 0.5 at%, and further preferably at 1.0 at%.

[0064] The upper limit of Co content is 49.0 at% as described above. The upper limit of Co content is preferably 30.0 at%, more preferably 15.0 at%, and furthermore preferably 10.0 at%. A lower limit of Co content is preferably 0.1 at%, more preferably 0.5 at%, and further preferably at 1.0 at%.

[0065] The upper limit of Ni content is 9.0 at% as described above. The upper limit of Ni content is preferably 5.0 at%, and more preferably 2.0 at%. A lower limit of Ni content is preferably 0.1 at%, more preferably 0.5 at%, and further preferably at 1.0 at%.

[0066] The upper limit of Zn content is 29.0 at% as described above. The upper limit of Zn content is preferably 27.0 at%, and more preferably 25.0 at%. A lower limit of Zn content is preferably 0.1 at%, more preferably 0.5 at%, and further preferably at 1.0 at%.

[0067] The upper limit of Al content is 49.0 at% as described above. The upper limit of Al content is preferably 30.0 at%, more preferably 15.0 at%, and furthermore preferably 10.0 at%. A lower limit of Al content is preferably 0.1 %, more preferably 0.5 at%, and further preferably at 1.0 at%.

[0068] The upper limit of Si content is 49.0 at% as described above. The upper limit of Si content is preferably 30.0 at%, more preferably 15.0 at%, and furthermore preferably 10.0 at%. A lower limit of Si content is preferably 0.1 at%, more preferably 0.5 at%, and further preferably at 1.0 at%.

[0069] The upper limit of B content is 5.0 at%. The lower limit of B content is preferably 0.01 at%, more preferably 0.1 at%, further preferably 0.5 at%, and furthermore preferably 1.0 at%.

[0070] A preferable upper limit of C content is 5.0 at%. The lower limit of C content is preferably 0.01 at%, more preferably 0.1 at%, further preferably 0.5 at%, and furthermore preferably 1.0 at%.

[0071] Preferably, the specific alloy phase contains one or more selected from the group consisting of δ phase of F-Cell structure containing site deficiency, ε phase of 2H structure containing site deficiency, η' phase of monoclinic crystal containing site deficiency, and a phase having $D0_3$ structure containing site deficiency. Hereinafter, these δ phase, ε phase, η' phase, and phase having $D0_3$ structure, each containing site deficiency is also referred to as "site deficient phase". Here, "site deficiency" means a state of a crystal structure in which occupancy factor is less than 1 in a specific atomic site.

[0072] These site deficient phases include a plurality of site deficiencies in the crystal structure. These site deficiencies function as a storage site or a diffusion site of metal ions (such as Li ions). Therefore, if a specific alloy phase contains an alloy phase which becomes 2H structure after M transformation and becomes $D0_3$ structure after reverse transformation, and at least one phase among the above described site deficient phases, the volumetric discharge capacity and the cycle characteristics of the negative electrode active material are further improved.

[0073] The chemical composition of a specific alloy phase may further contain a Group 2 element and/or rare earth metal (REM) for the purpose of increasing discharge capacity. The Group 2 elements include, for example, magnesium (Mg) calcium (Ca) and the like. REMs include, for example, lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd) and the like.

[0074] If a specific alloy phase contains a Group 2 element and/or REM, the negative electrode active material becomes brittle. Therefore, in the production process of the electrode, a bulk material or an ingot made of the negative electrode active material is easy to be pulverized, making it easy to produce an electrode.

[0075] The negative electrode active material may consist of the above described alloy phase and the ceramics dispersed in the alloy phase, or may contain another active substance phase which is metal-ion active besides the above described specific alloy phase and the ceramics. Another active material phase includes, for example, a tin (Sn) phase, a silicon (Si) phase, an aluminum (Al) phase, a Co-Sn alloy phase, a Cu_6Sn_5 compound phase (η' phase or η phase) and the like.

[Volume Expansion Ratio And Volume Contraction Ratio Of Specific Alloy Phase]

[0076] When the above described specific alloy phase undergoes M transformation or reverse transformation following occlusion and release of metal ions, preferable volume expansion/contraction ratio of unit cell of the specific alloy phase is not more than 20%. In this case, it is possible to sufficiently relax the strain due to a volume change which occurs following occlusion and release of metal ions. The volume expansion/contraction ratio of unit cell of the specific alloy phase is more preferably not more than 10%, and further preferably not more than 5%.

[0077] The volume expansion/contraction ratio of the specific alloy phase can be measured by an in-situ X-ray diffraction during charging/discharging. To be specific, an electrode plate of negative electrode active material, a separator, a counter electrode lithium, and electrolytic solution are placed and sealed in a dedicated charge/discharge cell including a window made of beryllium which transmits X-ray, within a glove box in pure argon gas atmosphere in which moisture is controlled such that due point is not more than -80°C. Then, this charge/discharge cell is mounted onto the X-ray diffraction apparatus. After mounting, an X-ray diffraction profile of the specific alloy phase is obtained in each of an initially charged state and an initially discharged state in the course of charging and discharging. From this X-ray diffraction profile, a lattice constant of the specific alloy phase is found. From the lattice constant, it is possible to calculate the volume change ratio in consideration of crystal lattice correspondence of the specific alloy phase.

[0078] When the shape of X-ray diffraction profile changes due to full width at half maximum etc. in the charge-discharge cycling process, analysis is performed after repeating charging and discharging 5 to 20 times as needed. Then, an average value of volume change ratio is found from a plurality of X-ray diffraction profiles having high reliability.

[Analysis Method Of Crystal Structure Of Alloy Phase Contained By Negative electrode active material]

[0079]

(1) The crystal structure of the phase (including an alloy phase) contained in the negative electrode active material can be analyzed by Rietveld method based on the X-ray diffraction profile obtained by using an X-ray diffraction apparatus. To be specific, the crystal structure is analyzed by the following method.

For a negative electrode active material before use for a negative electrode, X-ray diffraction measurement is performed on the negative electrode active material to obtain measured data of X-ray diffraction profile. Based on the obtained X-ray diffraction profile (measured data), the configuration of phases in the negative electrode active material is analyzed by Rietveld method. For the analysis by Rietveld method, either of "RIETAN2000" (program name) or "RIETAN-FP" (program name) which are general-purpose analysis software is used.

(2) The crystal structure of a negative electrode active material in a negative electrode before charging in a battery is determined by the same method as that in (1). To be specific, the battery, which is in an uncharged state, is disassembled within the glove box in argon atmosphere, and the negative electrode is taken out from the battery. The negative electrode taken out is enclosed with Myler foil. Thereafter, the perimeter of the Myler foil is sealed by a thermocompression bonding machine. Then, the negative electrode sealed by the Myler foil is taken out of the glove box.

Next, a measurement sample is fabricated by bonding the negative electrode to a reflection-free sample plate (a plate of a silicon single crystal which is cut out such that a specific crystal plane is in parallel with the measurement plane) with hair spray. The measurement sample is mounted onto the X-ray diffraction apparatus and X-ray diffraction measurement of the measurement sample is performed to obtain an X-ray diffraction profile. Based on the obtained X-ray diffraction profile, the crystal structure of the negative electrode active material in the negative electrode is determined by the Rietveld method.

(3) Crystal structures of the negative electrode active material in the negative electrode after charging one to multiple times and after discharging one to multiple times are determined by the same method as that in (2).

[0080] To be specific, the battery is fully charged in a charging/discharging test apparatus. The fully charged battery is disassembled in the glove box, and a measurement sample is fabricated by a method similar to that of (2). The measurement sample is mounted onto the X-ray diffraction apparatus and X-ray diffraction measurement is performed.

[0081] Moreover, the battery is fully discharged, and the fully discharged battery is disassembled in the glove box and a measurement sample is fabricated by a method similar to that of (2) to perform X-ray diffraction measurement.

[Ceramics]

[0082] The negative electrode active material according to embodiments of the present invention contains ceramics dispersed in a specific alloy phase. Containing ceramics will improve the capacity retention ratio, thereby improving the charge-discharge cycle characteristics. This is considered to be due to the following mechanism. For example, when charging and discharging are repeated multiple times such as not less than 100 cycles, cracking may occur in the specific alloy phase. The presence of ceramics dispersed in the alloy phase can suppress such cracking from propagating. Moreover, since ceramics does not relate to the charge-discharge reaction with metal ions such as lithium ion, it does not exhibit volume expansion/contraction at the time of charging and discharging. Therefore, it is considered that using the negative electrode active material relating to embodiments of the present invention improves the capacity retention ratio. It is desirable that the ceramics be uniformly dispersed.

[0083] The content of ceramics in the specific alloy phase is more than 0 to not more than 50 mass% with respect to the total mass of the specific alloy phase and the ceramics. The reason why to make the content to be not more than 50 mass% is to ensure a sufficient discharge capacity. The upper limit is more preferably not more than 10 mass%, and further preferably not more than 5 mass%. To sufficiently achieve the effect of suppressing crack propagation, the lower limit is more preferably not less than 0.01 mass%, and further preferably not less than 0.1 mass%.

[0084] Moreover, when a mechanical method such as mechanical grinding and mechanical alloying is used in the process of dispersing ceramics, strain is introduced into the specific alloy phase in the dispersion process. In this case, the diffusion/storage site of metal ion increases, thereby increasing electric capacity as the negative electrode active substance. However, the effect of capacity increase is restricted by the balance with the blending ratio of ceramics which is electrochemically inactive. As a matter of course, when the blending ratio of ceramics is high, its effect will become limited.

[0085] The average grain size of the ceramics contained and dispersed in the specific alloy phase is not particularly limited. Considering the effect of suppressing crack propagation, the average grain size of the ceramics is preferably 1 nm to 500 nm.

[0086] Preferably, the ceramics to be dispersed in the specific alloy phase is for example one or more kinds selected from the group consisting of Al_2O_3, FeSi, SiC, Si_3N_4, TiC, TiB_2, Y_2O_3, ZrB_2, HfB_2, ZrO_2, ZnO, WC, W_2C, CrB_2, BN, and $Ce0_2$. The reason why these ceramics are suitable for use in the negative electrode active material of the present embodiment is that its fine dispersion effect into the alloy is high. Particularly preferable ceramics is one or more kinds selected from the group consisting of Al_2O_3, FeSi, SiC, Si_3N_4, TiC, Y_2O_3, WC, and CeO_2.

<Production Method Of Negative Electrode Active material>

[0087] A negative electrode active material containing the above described specific alloy phase and a production method of a negative electrode and a battery using the negative electrode active material will be described.

[0088] A melt of the negative electrode active material containing the specific alloy phase (without containing ceramics) is produced. For example, molten metal having the above described chemical composition is produced. The molten

metal is produced by melting starting material by an ordinary melting method such as arc melting or resistance heating melting. Next, an ingot (bulk alloy) is produced by an ingot casting method by using the molten metal. By the above described processes, an alloy material as a material before ceramics is contained and dispersed (hereinafter, described simply as an "alloy material") is produced.

[0089] The alloy material is produced, preferably by subjecting the molten metal to rapid solidification. This method is called a rapid solidification method. Examples of the rapid solidification method include a strip casing method, a melt-spin method, a gas atomization method, a melt spinning method, a water atomization method, an oil atomization method, and the like.

[0090] When the alloy material is powdered, the bulk alloy (ingot) obtained by melting is (1) cut, (2) coarsely crushed by a hammer mill etc., or (3) finely pulverized mechanically by a ball mill, an attritor, a disc mill, a jet mill, a pin mill, and the like to be adjusted into a necessary grain size. When the bulk alloy has ductility and ordinary pulverization is difficult, the bulk alloy may be subjected to cutting and pulverization by a grinder disc, which is embedded with diamond abrasive particles, and the like. When M phase due to stress induction is formed in these pulverization processes, the formation ratio thereof is adjusted as needed by appropriately combining the alloy design, heat treatment, and pulverization conditions thereof. When powder generated by an atomization method can be used as melted or as heat treated, there may be cases where no pulverization process is particularly needed. Moreover, when melted material is obtained by a strip casting method and crushing thereof is difficult due to its ductility, the melted material is adjusted to have a predetermined size by being subjected to mechanical cutting such as shearing. Moreover, in such a case, the melted material may be heat treated in a necessary stage, to adjust the ratio between M phase and a matrix phase, and the like.

[0091] When the alloy material is heat treated to adjust the constitution ratio, etc. of the specific alloy phase, the alloy material may be rapidly cooled after being retained at a predetermined temperature for a predetermined time period in inert atmosphere as needed. In this occasion, the cooling rate may be adjusted by selecting a quenching medium such as water, salt water with ice, oil, and liquid nitrogen according to the size of the alloy material, and setting the quenching medium to a predetermined temperature.

[0092] Next, ceramics is dispersed in the above described alloy material (dispersion process). To disperse ceramics, a mechanical method is most effective. For example, the alloy material and the ceramic particles are charged into an instrument such as an attritor or a vibration ball mill, and the like, and the ceramics is dispersed in the alloy material through mechanical grinding effect or mechanical alloying effect. Preferable average grain size of the ceramic particles to be used is 1 nm to 500 nm as described above considering the effect of introduction of strain in the dispersion process. Performing mechanical alloying with the elements constituting the alloy material and the ceramics as the starting materials may be able to further enhance the dispersion effect. Through the above described processes, a negative electrode active material is produced.

<Production Method Of Negative Electrode>

[0093] A negative electrode using a negative electrode active material relating to an embodiment of the present invention can be produced by a method well known to those skilled in the art.

[0094] For example, a binder such as polyvinylidene fluoride (PVDF), polymethyl methacrylate (PMMA), polytetrafluoroethylene (PTFE), and styrene-butadiene rubber (SBR) is admixed to powder of a negative electrode active material of an embodiment of the present invention, and further carbon material powder such as natural graphite, artificial graphite, and acetylene black is admixed thereto to impart sufficient conductivity to the negative electrode. After being dissolved by adding a solvent such as N-methylpyrrolidone (NMP), dimethylformamide (DMF) and water, the binder is stirred well using a homogenizer and glass beads if necessary, and formed into a slurry. This slurry is applied on an active substance support member such as a rolled copper foil and an electrodeposited copper foil and is dried. Thereafter, the dried product is subjected to pressing. Through the above described processes, a negative electrode plate is produced.

[0095] The binder to be admixed is preferably about 5 to 10 mass% with respect to the mass of the entire slurry including the solvent from the viewpoints of mechanical strength and battery characteristics of the negative electrode. The support member is not limited to a copper foil. The support member may be, for example, a foil of other metals such as stainless steel and nickel, a net-like sheet punching plate, a mesh braided with a metal element wire and the like.

[0096] The particle size of the powder of negative electrode active material affects the thickness and density of electrode, that is, the capacity of electrode. The thickness of electrode is preferably as thin as possible. This is because a smaller thickness of electrode can increase the total surface area of the negative electrode active material included in a battery. Therefore, an average particle size of the powder of negative electrode active material is preferably not more than 100 μm. As the average particle size of the powder of negative electrode active material decreases, the reaction area of the powder increases, thereby resulting in excellent rate characteristics. However, when the average particle size of the powder of negative electrode active material is too small, the properties and condition of the surface of the powder change due to oxidation etc. so that it becomes difficult for lithium ions to enter into the powder. In such a case, the rate characteristics and the efficiency of charging/discharging may decline over time. Therefore, the average particle

size of the powder of negative electrode active material is preferably 0.1 to 100 μm, and more preferably 1 to 50 μm.

<Production Method Of Battery>

[0097] A nonaqueous electrolyte secondary battery according to the present embodiment includes a negative electrode, a positive electrode, a separator, and an electrolytic solution or electrolyte as described above. The shape of the battery may be a cylindrical type, a square shape as well as a coin type and a sheet type. The battery of the present embodiment may be a battery utilizing a solid electrolyte such as a polymer battery and the like.

[0098] The positive electrode of the battery of the present embodiment preferably contains a transition metal compound containing a metal ion as the active material. More preferably, the positive electrode contains a lithium (Li)-containing transition metal compound as the active material. An example of the Li-containing transition metal compound is LiM_1-$xM'xO_2$, or $LiM_2yM'O_4$. Where, in the chemical formulae, $0 \leq x$, $y \leq 1$, and M and M' are respectively at least one kind of barium (Ba), cobalt (Co), nickel (Ni), manganese (Mn), chromium (Cr), titanium (Ti), vanadium (V), iron (Fe), zinc (Zn), aluminum (Al), indium (In), tin (Sn), scandium (Sc) and yttrium (Y).

[0099] However, the battery of the present embodiment may use other positive electrode materials such as transition metal chalcogenides; vanadium oxide and lithium (Li) compound thereof; niobium oxide and lithium compound thereof; conjugated polymers using organic conductive substance; Shepureru phase compound; activated carbon; activated carbon fiber; and the like.

[0100] The electrolytic solution of the battery of the present embodiment is generally a nonaqueous electrolytic solution in which lithium salt as the supporting electrolyte is dissolved into an organic solvent. Examples of lithium salt include $LiClO_4$, $LiBF_4$, $LiPF_6$, $LiAsF_6$, $LiB(C_6H_5)$, $LiCF_3SO_3$, $LiCH_3SO_3$, $Li(CF_3SO_2)_2N$, $LiC_4F_9SO_3$, $Li(CF_2SO_2)_2$, LiCl, LiBr, and LiI. These may be used singly or in combination. The organic solvent is preferably carbonic ester, such as propylene carbonate, ethylene carbonate, ethyl methyl carbonate, dimethyl carbonate, and diethyl carbonate. However, other various kinds of organic solvents including carboxylate ester and ether are usable. These organic solvents may be used singly or in combination.

[0101] The separator is placed between the positive electrode and the negative electrode. The separator serves as an insulator. Further, the separator greatly contributes to the retention of electrolyte. The battery of the present embodiment may include a well known separator. The separator is made of, for example, polypropylene or polyethylene, which is polyolefin-based material, or mixed fabric of the two, or a porous body such as a glass filter. The above described negative electrode, positive electrode, separator, and electrolytic solution or electrolyte are accommodated in a container to produce a battery.

[0102] Hereinafter, the negative electrode active material, the negative electrode, and the battery of the present embodiment described above will be described in more detail by using Examples. It is noted that the negative electrode active material, the negative electrode, and the battery of the present embodiment will not be limited to Examples shown below.

EXAMPLES

[0103] Powdered negative electrode active materials, negative electrodes, and coin batteries of Inventive Examples 1 to 8 of the present invention and Comparative Examples 1 to 4 shown in Table 1 were produced by the following method. Then, changes in the crystal structure of each negative electrode active material caused by charging/discharging were confirmed. Further, discharge capacity (discharge capacity per volume) and cycle characteristics of each battery were investigated.

[Table 1]

[0104]

TABLE 1

	Alloy phase chemical composition	Ceramics			Battery characteristics		
		Composition	Ceramics content with respect to total amount of alloy phase and ceramics (weight%)	Average grain size (μm)	Initial discharge capacity (mAh/cm^3)	Discharge capacity at 100th cycle (mAh/cm^3)	Capacity retention ratio (%)
Inventive Example 1	(1) Cu-23at%Sn-5at%Si	Al_2O_3	1	0.06	2985	2745	92.0
Inventive Example 2	(1) Cu-23at%Sn-5at%Si	Al_2O_3	5	0.06	2741	2534	92.4
Inventive Example 3	(1) Cu-23at%Sn-5at%Si	Al_2O_3	45	0.06	1277	1123	87.9
Inventive Example 4	(1) Cu-23at%Sn-5at%Si	FeSi	1	16.3	2941	2694	91.6
Inventive Example 5	(1) Cu-23at%Sn-5at%Si	FeSi	5	16.3	2656	2434	91.6
Inventive Example 6	(1) Cu-23at%Sn-5at%Si	FeSi	45	16.3	1391	1354	97.3
Comparative Example 1	(1) Cu-23at%Sn-5at%Si	Al_2O_3	55	0.06	941	507	53.9
Comparative Example 2	(1) Cu-23at%Sn-5at%Si	-	-	-	1782	1502	84.3
Inventive Example 7	(2) Cu-20at%Sn-10at%Al	Al_2O_3	1	0.06	2977	2784	93.5
Comparative Example 3	(2) Cu-20at%Sn-10at%Al	-	-	-	1766	1455	82.4
Inventive Example 8	(3) Cu-25at%Sn	Al_2O_3	1	0.06	2865	2716	94.8
Comparative Example 4	(3) Cu-25at%Sn	-	-	-	1655	1313	79.3

[Inventive Example 1 Of The Present Invention]

[Production Of Negative electrode active material]

[0105] A mixture of a plurality of starting materials (elements) was high-frequency melted in a nozzle made of boron

nitride in argon gas atmosphere to produce molten metal in such a way that the final chemical composition of the negative electrode active material excepting the ceramics part becomes the chemical composition listed in the "chemical composition" column in Table 1. A rapidly solidified foil band was produced by spraying the molten metal onto a rotating copper roll in the alloy phase. The thickness of the foil band was 20 to 40 μm. This foil band was pulverized by a grinding machine (automatic mortar) into alloy powder of a size of not more than 45 μm. This alloy powder was used as the alloy material before the ceramics was contained and dispersed therein. The final chemical composition of the alloy phase in the negative electrode active material of Inventive Example 1 was as listed in the "chemical composition" column in Table 1, and contained 23 at% of Sn and 5 at% of Si, with the balance being Cu.

[0106] The alloy material was blended with ceramics of the kind and the grain size listed in Table 1 by the content listed in Table 1, and was subjected to dispersion treatment by a high-speed planetary mill (product name "High G" manufactured by KURIMOTO, LTD.). In this occasion, the mass proportion (ball ratio) between the raw material (total of the alloy material and the ceramics) as the source of the negative electrode active material and the ball was raw material: ball = 20 : 600. Moreover, the mill was operated for 12 hours in an argon inert gas atmosphere under a collision energy corresponding to 150 G.

[Production Of Negative Electrode]

[0107] The above powdered negative electrode active material, acetylene black (AB) as a conductive assistant, styrene-butadiene rubber (SBR) as a binder (2-fold dilution), and carboxymethylcellulose (CMC) as a thickening agent were mixed in a mass ratio of 75:15:10:5 (blending quantity was 1g: 0.2g: 0.134g: 0.067g). Then, a kneading machine was used to produce a negative electrode mixture slurry by adding distilled water to the mixture such that slurry density was 27.2%. Since the styrene-butadiene rubber was used by being diluted 2-fold with water, 0.134 g of styrene-butadiene rubber was blended when weighing.

[0108] The produced negative electrode mixture slurry was applied on a copper foil by using an applicator (150 μm). The copper foil applied with the slurry was dried at 100°C for 20 minutes. The copper foil after drying had a coating film made up of the negative electrode active material on the surface. The copper foil having the coating film was subjected to punching to produce a disc-shaped copper foil having a diameter of 13 mm. The copper foil after punching was pressed at a press pressure of 500 kgf/cm^2 to produce a plate-shaped negative electrode material.

[Production of Battery]

[0109] The produced negative electrode, EC-DMC-EMC-VC-FEC as the electrolytic solution, a polyolefin separator (ϕ17mm) as the separator, and a metal Li plate (ϕ19 × 1 mmt) as the positive electrode material were prepared. Thus prepared negative electrode, the electrolytic solution, the separator, and the positive electrode were used to produce a coin battery of 2016 type. Assembly of the coin battery was performed within a glove box in argon atmosphere.

[Determination Of Crystal Structure]

[0110] The crystal structures of the powdered negative electrode active material before using for the negative electrode, the negative electrode active material in the negative electrode before initial charging, and the negative electrode active material in the negative electrode after one to multiple times of charging and discharging were determined by the following method. The concerned negative electrode active materials were subjected to an X-ray diffraction measurement to obtain measured data. Then, based on the obtained measured data, crystal structures included in the target negative electrode active materials were determined by Rietveld method. More specifically, the crystal structures were determined by the following method.

(1) Crystal structure analysis of powdered negative electrode active material before use in negative electrode

[0111] X-ray diffraction measurements were carried out for the powder of the negative electrode active materials before use in the negative electrode to obtain measured data of X-ray diffraction profile.

[0112] To be specific, SmartLab (product of Rigaku Co., Ltd) (rotor target maximum output 9KW; 45kV-200mA) was used to obtain X-ray diffraction profiles of the powder of the negative electrode active materials.

[0113] Based on the obtained X-ray diffraction profiles (measured data), crystal structures of alloy phases in the negative electrode active material were analyzed by Rietveld method.

[0114] The $D0_3$ ordered structure is an ordered structure as shown in FIG. 2A. In a Cu-Sn base alloy, mainly Cu is present at atomic sites shown by a black circle and mainly Sn is present at atomic sites shown by a white circle, in FIG. 2A. Respective sites may be replaced by addition of a third element. It is known that such a crystal structure falls into No. 225 (Fm-3m) of International Table (Volume-A) in the classification of space group representation. The lattice

constant and atomic coordinates of this space group number are as shown in Table 2.

[Table 2]

[0115]

TABLE 2

Parent phase (β_1 Phase), Crystal Structure: $D0_3$ Space Group Number (International Table A): No.225 (Fm-3m) Lattice Constant: a = 6.05 Å					
Site Name	Atomic Species	Multiplicity/Wyckoff Symbol	Atomic Coordinates		
			x	y	z
Sn1	Sn	4a	0.0	0.0	0.0
Cu1	Cu	8c	1/4	1/4	1/4
Cu2	Cu	4b	1/2	1/2	1/2

[0116] Accordingly, with the structure model of this space group number being as the initial structure model of Rietveld analysis, a calculated value of diffraction profile (hereinafter, referred to as a calculated profile) of β_1 phase ($D0_3$ structure) of this chemical composition was found by Rietveld method. RIETAN-FP (program name) was used for Rietveld analysis.

[0117] Further, a calculated profile of the crystal structure of γ_1' phase was found as well. The crystal structure of γ_1'was 2H structure in the notation of Ramsdell symbol, and the space group was No. 59-2 (Pmmn) of International Table (Volume-A). The lattice constant and atomic coordinates of No. 59-2 (Pmmn) are shown in Table 3.

[Table 3]

[0118]

TABLE 3

M Phase (γ_1' Phase), Crystal Structure: 2H Space Group Number (International Table A): No.59-2 (Pmmn) Lattice Constants: a = 4.379 Å, b = 5.498 Å, c = 4.615 Å					
Site Name	Atomic Species	Multiplicity/Wyckoff Symbol	Atomic Coordinates		
			x	y	z
Sn1	Sn	2b	1/4	3/4	1/6
Cu1	Cu	2a	1/4	1/4	1/6
Cu2	Cu	4e	1/4	0.0	2/3

[0119] A calculated profile was found by using RIETAN-FP supposing that the crystal structure of the space group number of the above describe Table 3 be the initial structure model of Rietveld analysis.

[0120] A result of the analysis revealed that a γ_1' phase (2H structure) which is a kind of M phase, and a β_1 phase ($D0_3$ tructure) which is the matrix phase of the γ_1' phase (2H structure) were intermixed in the negative electrode active material of Inventive Example 1.

(2) Crystal Structure Analysis Of Negative electrode active material In Negative Electrode

[0121] The crystal structure of a negative electrode active material in a negative electrode before charging was also determined by the same method as that in (1). A measured X-ray diffraction profile was measured by the following method.

[0122] The above described coin battery, which was before being charged, was disassembled within the glove box in argon atmosphere, and a plate-shaped negative electrode was taken out from the coin battery. The negative electrode taken out was enclosed in Myler foil (manufactured by DuPont). Thereafter, the perimeter of the Myler foil was sealed by a thermocompression bonding machine. Then, the negative electrode sealed by the Myler foil was taken out of the

glove box.

[0123] Next, a measurement sample was fabricated by bonding the negative electrode to a reflection-free sample plate manufactured by Rigaku Co., Ltd. (a plate of a silicon single crystal which was cut out such that a specific crystal plane was in parallel with the measurement plane) with a hair spray.

[0124] The measurement sample was mounted onto the X-ray diffraction apparatus described below in (4), and the X-ray diffraction measurement of the measurement sample was performed under measurement conditions described below in (4).

(3) Analysis Of Crystal Structure Of Negative electrode active material In Negative Electrode After Charging And After Discharging

[0125] The crystal structure of the negative electrode active material in the negative electrode after one to 100 times of charging and after one to 100 times of discharging was also determined by the same method as that in (1). The measured X-ray diffraction profile was measured by the following method.

[0126] The above described coin battery was fully charged in a charging/discharging test apparatus. The fully charged coin battery was disassembled in the glove box, and a measurement sample was fabricated by the same method as that in (2). The measurement sample was mounted onto the X-ray diffraction apparatus described below in (4), and X-ray diffraction measurement of the measurement sample was performed under measurement conditions described below in (4).

[0127] Moreover, the above described coin battery was fully discharged. The fully discharged coin battery was disassembled in the glove box, and a measurement sample was fabricated by the same method as in (3). The measurement sample was mounted onto the X-ray diffraction apparatus described below in (4), and X-ray diffraction measurement of the measurement sample was performed at measurement conditions described below in (4).

[0128] For a negative electrode which had been subjected to charging and discharging repeatedly in a coin battery, X-ray diffraction measurement was performed by the same method.

(4) X-Ray Diffraction Apparatus And Measurement Conditions

[0129]

- Apparatus: SmartLab manufactured by Rigaku Co., Ltd.
- X-ray tube: Cu-Kα ray
- X-ray output: 45 kV, 200 mA
- Incident monochrometer: Johannson-type crystal (which filters out Cu-Kα_2 ray and Cu-Kβ ray)
- Optical system: Bragg-Brentano geometry
- Incident parallel slit: 5.0 degrees
- Incident slit: 1/2 degree
- Length limiting slit: 10.0 mm
- Receiving slit 1: 8.0 mm
- Receiving slit 2: 13.0 mm
- Receiving parallel slit: 5.0 degrees
- Goniometer: SmartLab goniometer
- X-ray source - mirror distance: 90.0 mm
- X-ray source - selection slit distance: 114.0 mm
- X-ray source - sample distance: 300.0 mm
- Sample - receiving slit 1 distance: 187.0 mm
- Sample - receiving slit 2 distance: 300.0 mm
- Receiving slit 1 - receiving slit 2 distance: 113.0 mm
- Sample - detector distance: 331.0 mm
- Detector: D/Tex Ultra
- Scan range: 10 to 120 degrees or 10 to 90 degrees
- Scan step: 0.02 degrees
- Scan mode: Continuous scan
- Scanning speed: 2 degrees/min or 2.5 degrees/min

(5) Analysis results of X-ray diffraction measurement data

(5-1)

[0130] From X-ray diffraction data obtained in (1), (2), and (3), it can be confirmed that no significant reaction has occurred between the negative electrode active material and the electrolytic solution.

(5-2)

[0131] The X-ray diffraction profiles of "negative electrode active material after charging" and "negative electrode active material after discharging" revealed that the diffraction lines repeatedly changed in a reversible manner at a position where the diffraction angle 2θ is near 37.5 to 39.0° (position caused by M phase (γ_1' phase)) (hereinafter, referred to as a major diffraction line position). That is, structural changes were suggested.

(5-3)

[0132] Accordingly, the crystal structures of the "negative electrode active material after charging" and the "negative electrode active materials after discharging" were determined by using Rietveld method.

[0133] For example, in the negative electrode active material, the crystal plane A shown in FIG. 2D and the crystal plane B shown in FIG. 2C are alternately layered in the $D0_3$ structure of the matrix phase shown in FIGS. 1 and 2A. When a phase transformation occurs between the $D0_3$ structure and γ_1' phase which is a kind of M phase, as shown in FIGS. 2A and 2B, the crystal plane B regularly undergoes shuffling due to shear stress, thereby being displaced to the position of crystal plane B'. In this case, phase transformation (M transformation) occurs without diffusion of the host lattice. In the 2H structure after M transformation, the crystal plane A shown in FIG. 2D and the crystal plane B' shown in FIG. 2E are alternately layered.

[0134] Then, it was judged whether the crystal structure of the negative electrode active material in the negative electrode of the present example involved M transformation or was not accompanied thereby (that is, involved diffusion of host lattice at the time of charging/discharging) by comparing the measured data of the X-ray diffraction profiles of the negative electrode active material after charging and after discharging, the calculated profile of β_1 phase ($D0_3$ structure), and the calculated profile of γ_1' phase (2H structure).

[0135] In the X-ray diffraction profile, the intensity of the diffraction line of near 37.5° to 39.9° increased as a result of initial charging, and decreased as a result of consecutive discharging. It can be judged that this diffraction line resulted from the formation of M phase (γ_1') by M transformation, as will be next described, from calculated profiles of RIETAN-FP).

[0136] To be specific, in the 2H structure, an intensity peak appeared at 37.5 to 39.0° of the X-ray diffraction profile. On the other hand, in the $D0_3$ structure, no intensity peak appeared at 37.5 to 39.0°. In contrast to this, in the X-ray diffraction profile after charging, an intensity peak appeared at 37.5 to 39.0°. On the other hand, in the X-ray diffraction profile after discharging, no intensity peak appeared at 37.5 to 39.0°. Further, the intensity peak at 37.5 to 39.0° did not appear in the X-ray profile (simulation result) of any crystal structure other than 2H. Here, the reason why the angle range of the diffraction line is as wide as 37.5 to 39.0° as stated above was that due to the effect of the mechanical grinding (MG) in the ceramics dispersion process, strain was introduced in the material, thus resulting in increase in the half value width.

[0137] From the above, the negative electrode of the present Example contained an alloy phase which underwent M transformation to become M phase (2H structure) as a result of charging, and became a matrix phase ($D0_3$ structure) as a result of discharging. That is, the negative electrode of the present Example contained an alloy phase which underwent M transformation when occluding lithium ions which are metal ions, and underwent reverse transformation when releasing lithium ions.

[0138] In the negative electrode of the present Example, M transformation at the time of charging, and reverse transformation at the time of discharging were repeated.

[Charge-Discharge Performance Evaluation Of Coin Battery]

[0139] Next, discharge capacity and cycle characteristics of the battery of Inventive Example 1 were evaluated.

[0140] Constant current doping (corresponding to the insertion of lithium ions into electrode, and the charging of lithium ion secondary battery) was performed to a coin battery at a current value of 0.1 mA (a current value of 0.075 mA/cm^2) or a current value of 1.0 mA (a current value of 0.75 mA/cm^2) until the potential difference against the counter electrode becomes 0.005 V. Thereafter, doping capacity was measured by continuing doping against the counter electrode at a constant voltage until the current value became 7.5 μA/cm^2 while retaining 0.005 V.

[0141] Next, de-doping capacity was measured by performing de-doping (which corresponds to desorption of lithium

ions from the electrode, and discharge of the lithium ion secondary battery) at a current value of 0.1 mA (a current value of 0.075 mA/cm^2) or a current value of 1.0 mA (a current value of 0.75 mA/cm^2) until the potential difference becomes 1.2 V.

[0142] The doping capacity and de-doping capacity correspond to charge capacity and discharge capacity when the electrode is used as the negative electrode of the lithium ion secondary battery. Therefore, the measured dope capacity was defined as the charge capacity, and a measured de-doping capacity was defined as the discharge capacity.

[0143] Charging and discharging were repeated 100 times at the same conditions as described above. Then, a capacity retention ratio (%) was defined as "the discharge capacity at the time of de-doping of the 100th cycle" divided by "the discharge capacity at the time of de-doping of the 1st cycle, and multiplied by 100. In the coin battery of Inventive Example 1, the initial discharge capacity, the discharge capacity of the 100th cycle, and the capacity retention ratio were as listed in Table 1.

[Inventive Examples 2 and 3]

[0144] In Inventive Examples 2 and 3, negative electrode active materials, negative electrodes, and coin batteries were produced in the same way as in Inventive Example 1 excepting that the ceramics contents were changed as shown in Table 1.

[0145] Determination of crystal structure, and evaluation of oxygen concentration in the negative electrode active material and various charge-discharge performances of the coin battery were performed in the same way as in Inventive Example 1.

[0146] The result of the determination of crystal structure was the same as in Inventive Example 1. That is, it was confirmed that the alloy phases of Inventive Examples 2 and 3 had a crystal structure that undergoes M transformation when occluding lithium ions, and undergoes reverse transformation when releasing lithium ions. The results of the evaluation of various charge-discharge performances of the coin battery were as shown in Table 1.

[Inventive Examples 4 to 6]

[0147] In Inventive Examples 4 to 6, negative electrode active materials, negative electrodes, and coin batteries were produced in the same way as in Inventive Example 1 excepting that the kinds, the contents, and the average grain sizes before being charged into an attritor mill of the ceramics were changed as shown in Table 1.

[0148] Determination of crystal structure, and evaluation of various charge-discharge performances of the coin battery were performed in the same way as in Inventive Example 1. The result of the determination of crystal structure was the same as in Inventive Example 1. That is, it was confirmed that the alloy phases of Inventive Examples 4 to 6 had a crystal structure that undergoes M transformation when occluding lithium ions, and undergoes reverse transformation when releasing lithium ions. Results of the evaluation of various charge-discharge performances of the coin battery were as shown in Table 1.

[Comparative Examples 1 and 2]

[0149] In Comparative Example 1, the negative electrode active material, negative electrode, and coin battery were produced in the same way as in Inventive Example 1 excepting that the content of ceramics was changed as shown Table 1. In Comparative Example 2, the negative electrode and coin battery were produced in the same way as in Inventive Example 1 excepting that the alloy material obtained by pulverization with the grinding machine (automatic mortar) in Inventive Example 1 was used as the negative electrode active material. The negative electrode active material of Comparative Example 2 did not contain ceramics.

[0150] Determination of crystal structure, and evaluation of various charge-discharge performances of the coin battery were performed in the same way as in Inventive Example 1. The result of the determination of crystal structure was the same as in Inventive Example 1. That is, it was confirmed that the alloy phases of Comparative Examples 1 and 2 had a crystal structure that undergoes M transformation when occluding lithium ions, and undergoes reverse transformation when releasing lithium ions. The results of evaluation of various charge-discharge performances of the coin battery were as shown in Table 1.

[Inventive Example 7 and Comparative Example 3]

[0151] In Inventive Example 7, the negative electrode active material, negative electrode, and coin battery were produced in the same way as in Inventive Example 1 excepting that the final chemical composition of the alloy phase was changed to the composition according to Table 1.

[0152] In Comparative Example 3, the negative electrode and coin battery were produced in the same way as in Inventive Example 7 excepting that the alloy material obtained by pulverization with the grinding machine (automatic

mortar) in Inventive Example 7 was used as the negative electrode active material. The negative electrode active material of Comparative Example 3 did not contain any ceramics.

[0153] Determination of crystal structure, and evaluation of various charge-discharge performances of the coin battery were performed in the same way as in Inventive Example 1. The result of the determination of crystal structure was the same as in Inventive Example 1. That is, it was confirmed that the alloy phases of Inventive Examples 7 and Comparative Example 3 had a crystal structure that undergoes M transformation when occluding lithium ions, and undergoes reverse transformation when releasing lithium ions. The results of evaluation of various charge-discharge performances of the coin battery were as shown in Table 1.

[Inventive Example 8 and Comparative Example 4]

[0154] In Inventive Example 8, the negative electrode active material, negative electrode, and coin battery were produced in the same way as in Inventive Example 1 excepting that the final chemical composition of the alloy phase was changed to the composition according to Table 1.

[0155] In Comparative Example 4, the negative electrode and coin battery were produced in the same way as in Inventive Example 8 excepting that the alloy material obtained by pulverization with the grinding machine (automatic mortar) in Inventive Example 8 was used as the negative electrode active material. The negative electrode active material of Comparative Example 4 did not contain any ceramics.

[0156] Determination of crystal structure, and evaluation of various charge-discharge performances of the coin battery were performed in the same way as in Inventive Example 1. According to the determination of crystal structure, the alloy phase changed as follows as charging/discharging was performed. The alloy phase was M phase (2H structure) before initial charging, M phase (2H structure) after initial charging, and a matrix phase ($D0_3$ structure) after initial discharging, and thereafter, the alloy phase underwent M transformation to be transformed into M phase (2H structure) through charging, and became matrix phase ($D0_3$ structure) through discharging. That is, it was confirmed that the negative electrodes of Inventive Examples 8 and Comparative Example 4 had an alloy phase that undergoes M transformation when occluding lithium ions which are metal ions, and undergoes reverse transformation when releasing lithium ions. Results of evaluating various charge-discharge performances of the coin battery were as shown in Table 1.

[0157] With reference to Table 1, in each of Inventive Examples 1 to 8, the content of ceramics with respect to the total mass of the alloy phase of the ceramics was more than 0 to 50 mass%. As a result of that, the discharge capacities at the initial and the 100th cycles were as high as not less than 1100 mAh/cm^3 and the capacity retention ratio was not less than 85% as well.

[0158] On the other hand, in Comparative Example 1, the ceramics content was more than 50 mass%. As a result of that, the discharge capacity was low, and the capacity retention ratio was less than 90% as well. In Comparative Examples 2 to 4, the ceramics was not contained. As a result of that the capacity retention ratio was less than 90%.

[0159] So far, embodiments of the present invention have been described. However, the above described embodiments are merely examples to carry out the present invention, which is defined by the appended claims.

Claims

1. A negative electrode active material comprising an alloy phase, wherein the alloy phase contains: Sn: 10 to 35 at%; and one or more kinds selected from the group consisting of Ti: 9.0 at% or less, V: 49.0 at% or less, Cr: 49.0 at% or less, Mn: 9. 0 at% or less, Fe: 49.0 at% or less, Co: 49.0 at% or less, Ni: 9.0 at% or less, Zn: 29.0 at% or less, Al: 49.0 at% or less, Si: 49.0 at% or less, B: 5.0 at% or less, and C: 5.0 at% or less,with the balance being Cu and impurities; and **characterized in that** the negative electrode active material further comprises ceramics dispersed in the alloy phase, wherein the content of the ceramics in the alloy phase is more than 0 to 50 mass% with respect to a total mass of the alloy phase and the ceramics.

2. A negative electrode active material, comprising:

   an alloy phase which undergoes thermoelastic diffusionless transformation when releasing metal ions or occluding the metal ions;
   wherein
   the alloy phase undergoes thermoelastic diffusionless transformation when occluding the metal ions, and undergoes reverse transformation when releasing the metal ions, wherein
   the alloy phase after the thermoelastic diffusionless transformation contains a crystal structure which is 2H in Ramsdell notation, and
   the alloy phase after the reverse transformation contains a crystal structure which is $D0_3$, in Strukturbericht

notation, **characterized in that** either the alloy phase contains:

(i) 10 to 20 at% or 21 to 27 at% of Sn, with the balance being Cu and impurities, and ceramics dispersed in the alloy phase, wherein the content of the ceramics in the alloy phase is more than 0 to 50 mass% with respect to a total mass of the alloy phase and the ceramics; or
ii) the active material is a negative electrode active material according to claim 1.

3. The negative electrode active material according to claim 2, wherein the ceramics contains one or more kinds selected from the group consisting of Al_2O_3, FeSi, SiC, Si_3N_4, TiC, TiB_2, Y_2O_3, ZrB_2, HfB_2, ZrO_2, ZnO, WC, W_2C, CrB_2, BN, and CeO_2.

4. A negative electrode, comprising the negative electrode active material according to any one of claims 2 or 3.

5. A battery, comprising the negative electrode according to claim 4.

Patentansprüche

1. Aktives Material der negativen Elektrode, umfassend eine Legierungsphase, wobei die Legierungsphase Folgendes enthält: Sn: 10 bis 35 Atom-%; und eine oder mehrere Arten, ausgewählt aus der Gruppe bestehend aus Ti: 9,0 Atom-% oder weniger, V: 49,0 Atom-% oder weniger, Cr: 49,0 Atom-% oder weniger, Mn: 9, 0 Atom-% oder weniger, Fe: 49,0 Atom-% oder weniger, Co: 49,0 Atom-% oder weniger, Ni: 9,0 Atom-% oder weniger, Zn: 29,0 Atom-% oder weniger, Al: 49,0 Atom-% oder weniger, Si: 49,0 Atom-% oder weniger, B: 5,0 Atom-% oder weniger und C: 5,0 Atom-% oder weniger, wobei der Rest Cu und Verunreinigungen ist; und **dadurch gekennzeichnet, dass** das aktive Material der negativen Elektrode ferner Keramik umfasst, die in der Legierungsphase dispergiert ist, wobei der Gehalt der Keramik in der Legierungsphase mehr als 0 bis 50 Massen-% in Bezug auf eine Gesamtmasse der Legierungsphase und der Keramik ist.

2. Aktives Material der negativen Elektrode, umfassend:

eine Legierungsphase, die einer thermoelastischen diffusionslosen Umwandlung unterzogen wird, wenn Metallionen freigesetzt werden oder die Metallionen okkludiert werden;
wobei
die Legierungsphase thermoelastischer diffusionsloser Umwandlung unterzogen wird, wenn die Metallionen eingeschlossen werden, und einer Rückumwandlung unterzogen wird, wenn die Metallionen freigesetzt werden,
wobei
die Legierungsphase nach der thermoelastischen diffusionslosen Umwandlung eine Kristallstruktur enthält, die 2H in der Ramsdell-Notation ist, und
die Legierungsphase nach der Rückumwandlung eine Kristallstruktur enthält, die $D0_3$ in Strukturbericht-Notation ist, **gekennzeichnet dadurch, dass** die die Legierungsphase entweder Folgendes enthält:

(i) 10 bis 20 Atom-% der 21 bis 27 Atom-% Sn, wobei der Rest Cu und Verunreinigungen ist, und Keramik, die in der Legierungsphase dispergiert ist, wobei der Gehalt der Keramik in der Legierungsphase mehr als 0 bis 50 Massen-% in Bezug auf eine Gesamtmasse der Legierungsphase und der Keramik ist; oder
ii) das aktive Material ein aktives Material der negativen Elektrode nach Anspruch 1 ist.

3. Aktives Material der negativen Elektrode nach Anspruch 2, wobei
die Keramik eine oder mehrere Arten enthält, ausgewählt aus der Gruppe bestehend aus Al_2O_3, FeSi, SiC, Si_3N_4, TiC, TiB_2, Y_2O_3, ZrB_2, HfB_2, ZrO_2, ZnO, WC, W_2C, CrB_2, BN und $Ce0_2$.

4. Negative Elektrode, umfassend das aktive Material der negativen Elektrode nach einem der Ansprüche 2 oder 3.

5. Batterie, umfassend die negative Elektrode nach Anspruch 4.

Revendications

1. Matériau actif d'électrode négative, comprenant une phase d'alliage, dans lequel la phase d'alliage contient : Sn :

de 10 à 35 % atomique ; et un ou plusieurs types sélectionnés parmi le groupe constitué de Ti : 9,0 % atomique ou moins, V : 49,0 % atomique ou moins, Cr : 49,0 % atomique ou moins, Mn : 9, 0 % atomique ou moins, Fe : 49,0 % atomique ou moins, Co : 49,0 % atomique ou moins, Ni : 9,0 % atomique ou moins, Zn : 29,0 % atomique ou moins, Al : 49,0 % atomique ou moins, Si : 49,0 % atomique ou moins, B : 5,0 % atomique ou moins, et C : 5,0 % atomique ou moins, le reste étant Cu et des impuretés ; et **caractérisé en ce que** le matériau actif d'électrode négative comprend en outre de la céramique dispersée dans la phase d'alliage, dans lequel la teneur en céramique dans la phase d'alliage est supérieure à 0 à 50 % massique par rapport à une masse totale de la phase d'alliage et de la céramique.

2. Matériau actif d'électrode négative, comprenant :

une phase d'alliage qui subit une transformation sans diffusion thermoélastique lors de la libération d'ions métalliques ou de l'occlusion des ions métalliques ;
dans lequel
la phase d'alliage subit une transformation sans diffusion thermoélastique lors de l'occlusion des ions métalliques, et subit une transformation inverse lors de la libération des ions métalliques, dans lequel
la phase d'alliage après la transformation sans diffusion thermoélastique contient une structure cristalline qui est 2H en notation Ramsdell, et
la phase d'alliage après la transformation inverse contient une structure cristalline qui est $D0_3$, en notation Strukturbericht, **caractérisé en ce que** la phase d'alliage contient :

i) de 10 à 20 % atomique ou de 21 à 27 % atomique de Sn, le reste étant Cu et des impuretés, et de la céramique dispersée dans la phase d'alliage, dans lequel la teneur en céramique dans la phase d'alliage est supérieure à 0 à 50 % massique par rapport à une masse totale de la phase d'alliage et de la céramique ; ou
ii) le matériau actif est un matériau actif d'électrode négative selon la revendication 1.

3. Matériau actif d'électrode négative selon la revendication 2, dans lequel
la céramique contient un ou plusieurs types sélectionné parmi le groupe constitué de : Al_2O_3, FeSi, SiC, Si_3N_4, TiC, TiB_2, Y_2O_3, ZrB_2, HfB_2, ZrO_2, ZnO, WC, W_2C, CrB_2, BN, et $Ce0_2$.

4. Électrode négatif, comprenant le matériau actif d'électrode négative selon l'une quelconque des revendications 2 ou 3.

5. Batterie, comprenant l'électrode négative selon la revendication 4.

FIG. 1

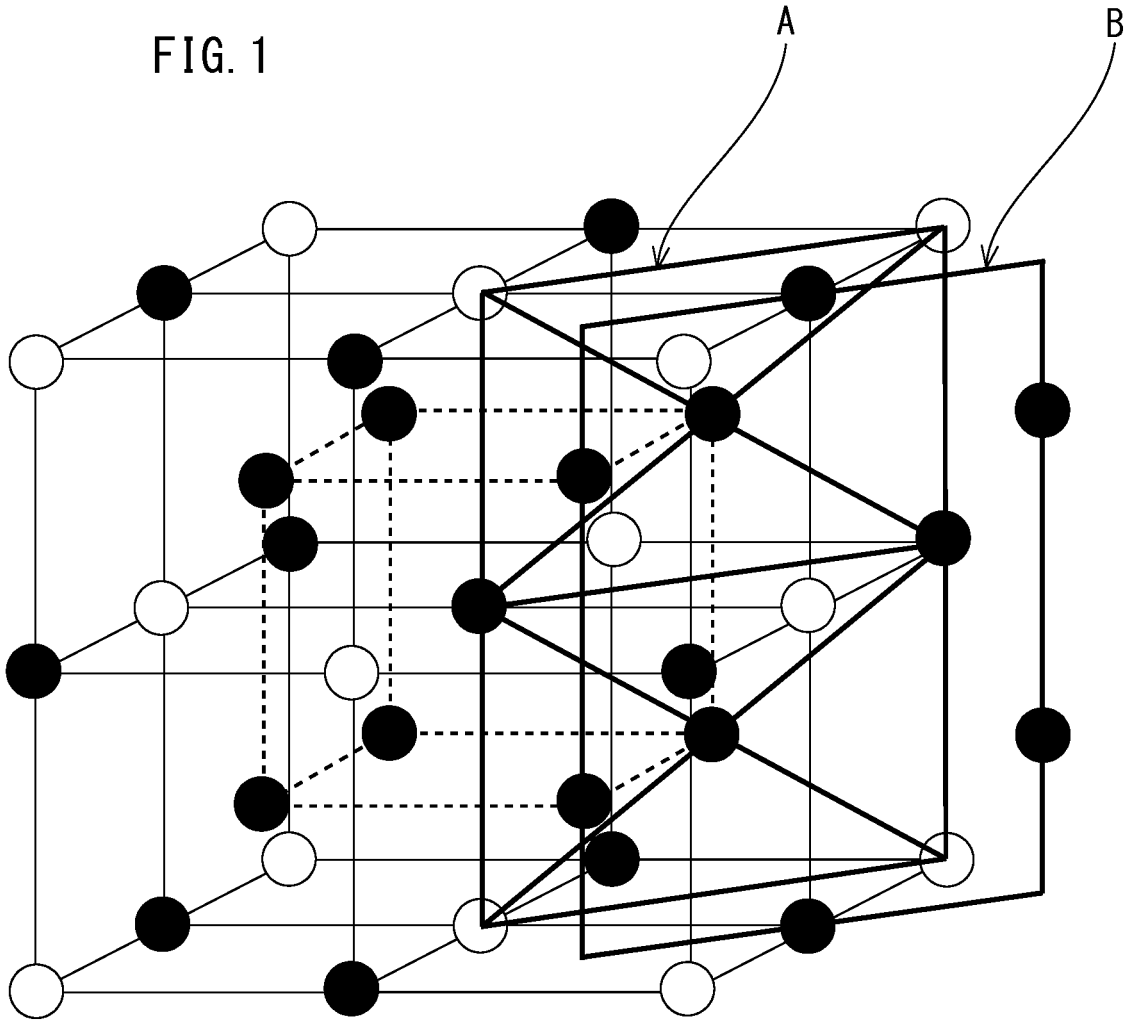


FIG. 2A

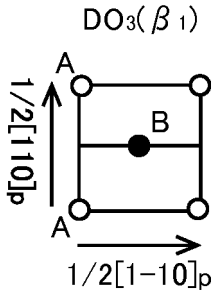


FIG. 2B

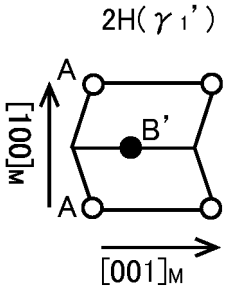


FIG. 2C

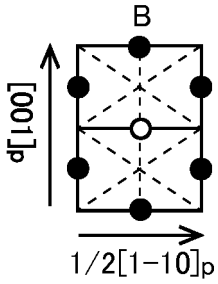


FIG. 2D

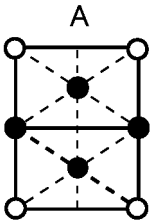
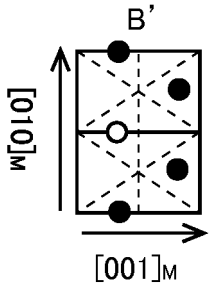


FIG. 2E



REFERENCES CITED IN THE DESCRIPTION

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